

Synthesis and Characterization of Tetraoxime Ligand, Bis-[(2E,3E,2'E)-3,3'-(1,2-Phenylene-Dinitrilo)dibutan-2- One Dioxime] and Its Dinuclear and Tetranuclear Copper(II)/Nickel(II) Complexes

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A new tetraoxime, (H_4L), was prepared in EtOH by reacting biphenyl-3,3',4,4'-tetramine with butane-2,3-dione oxime. The tetraoxime ligand was characterized by elemental analyses, 1H -NMR and ^{13}C -NMR, IR, and mass spectral studies. Dinuclear copper(II), nickel(II) and tetranuclear copper(II) complexes of tetraoxime ligand were prepared and characterized by elemental analyses, magnetic moments, IR, and mass spectral studies. In the dinuclear metal complexes, metal:ligand ratio was found as 2:1. Elemental analyses and stoichiometric and spectroscopic data of the metal complexes indicated that the metal ions were coordinated to the nitrogen atoms of oxime groups ($C=N$). In addition, total energy and heat formation for ligand and dinuclear Cu(II)/Ni(II) complexes by semiempirical PM3 calculations show that square-planar geometry is more stable than other geometries.

Key Words: Tetraoxime dinuclear, tetranuclear, copper and nickel complexes.

Introduction

The copper(II) and nickel(II) complexes have been extensively studied in recent years.¹⁻⁴ During the last decade, great attention was given to the area of multinuclear complexes with extended bridges,^{5,6} mainly because of the need to gain insight into the electron transfer pathways in biological systems.⁷ Several metal complexes have

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been synthesized in order to obtain detailed information about the exchange mechanism in these systems since biomolecules with multinuclear metal centres are known to be involved in important biological processes, such as catalysis.^{8,9} The homomultinuclear copper complexes of macrocyclic or macroacyclic ligands have been reported to undergo redox reactions similar to the active site in several metalloproteins and they were also proved to be efficient catalysts under mild conditions.^{10–12} In order to elucidate the factors that determine the function and activation of metalloproteins, several works have focused on the understanding of the correlation between the active site of metalloproteins with their metalcenters.^{13,14} A number of dinuclear complexes from various type ligand systems have been prepared and examined in terms of their oxygen uptake^{14–23} or redox processes.^{24–27} In addition, dinucleating macrocycles have been synthesized by combining chelating acyclic subunits²⁸ or by functionalizing a macrocyclic structure by attaching side chains.^{29,30} It has been reported that the derivatized macrocyclic systems exhibited the characteristics of mono- and dinuclear complexes, such as catalysis and molecular recognition.^{12, 31,32}

We investigated the synthesis and characterization of various transition metal complexes of novel Schiff bases and/or oximes^{1–4} in our previous studies. In this study, a new tetraoxime ligand, bis-[(2E,3E,2'E)-3,3'-(1,2-phenylene-dinitrilo)dibutan-2-one dioxime] (H₄L) has been characterized by elemental analyses, ¹H-NMR, ¹³C-NMR, IR and mass spectral studies, magnetic susceptibility, and semiempirical PM3 calculations.

Experimental

¹H-NMR, ¹³C-NMR spectra were recorded on a Varian Gemini 200 spectrometer using DMSO-d₆ as solvent. Chemical shifts (δ) were reported in p.p.m. relative to Me₄Si using the solvent signal as an internal reference. C, H, and N contents were determined microanalytically on a CHNS Costech 4010 analyzer, and metal contents were estimated spectrophotometrically. IR spectra were recorded on an ATI Unicam Matson 1000 Model FTIR spectrophotometer and Uv-Vis spectra on an ATI Unicam UV2 Model UV/Vis spectrophotometer. Mass spectra (ESI) were recorded on a Micromass Quattro LC-MS/MS spectrophotometer. Room temperature magnetic susceptibility measurements were performed on a PAR model 155 vibrating sample magnetometer. The Smart Minimizer was used for energy minimization, which was a combination of methods, starting with the Steepest Descent Method, followed by the Fletcher-Reeves and Block-diagonal Newton-Raphson methods, and ending with the accurate Polak-Ribiere method. The semiempirical PM3 calculations used MOPAC/PM3 version 8.0, including electronic properties, optimized geometries, total energy, dipole moment, and heat of formation as known as SCF method.³³

Synthesis of ligand (3)

3,3'-diamino benzidine (2.14 g, 10 mmol) dissolved in 25 mL absolute EtOH and 2,3-butene-dione monoxime (4.2 g, 40 mmol) dissolved in 20 mL absolute EtOH were mixed together. This mixture was refluxed with stirring for 4 h. The resulting brown solution was filtered while hot and concentrated slowly. As this solution cooled, a dark brown crystalline product precipitated. This product was isolated by vacuum filtration, and washed with EtOH and Et₂O, in that order. Then this pale brown solid product was dried in open air. Yield 4 g (73%). m.p. 262 °C. Ms: (ESI) m/z 546.64(10) [M]⁺, 392.41(10), 316.40(30), 315.45(100), 130.19(15). Anal. Calcd (found) for C₂₈H₃₄N₈O₄: C, 61.54 (61.50); H, 6.23 (6.15); N, 20.51 (20.40).

Synthesis of $[\text{Ni}_2(\text{H}_2\text{L})](\text{ClO}_4)_2$, (4)

A solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (731 mg, 2 mmol) in dried EtOH (10 mL) was added to the ligand solution (546 mg, 1 mmol) in 25 mL of EtOH, and this mixture was refluxed with stirring for 3 h. The resulting brown solid product was filtered-off, and then washed with EtOH and Et_2O , in that order. Then the red solid product (yield: 0.5 g, 58%) was dried in vacuum. Ms: (ESI) m/z 862.73(861) $[\text{M}+1]^+$ Anal. Calcd (found) for $\text{C}_{28}\text{H}_{32}\text{N}_8\text{O}_{12}\text{Cl}_2\text{Ni}_2$: C, 39.02 (39.12); H, 3.71 (3.65); N, 13.0 (12.95); Ni, 13.59 (13.55).

Synthesis of $[\text{Cu}_2[\text{H}_2\text{L}](\text{ClO}_4)_2$, (5)

A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (750 mg, 2 mmol) in dried EtOH (10 mL) was added to the ligand solution (546 mg, 1 mmol) in 25 mL of EtOH, and this mixture was refluxed with stirring for 3 h. The resulting green-brown solution was filtered when it was hot, and concentrated slowly. As the solution cooled, a pale green crystalline product precipitated. The green product was filtered off, and then washed with EtOH and Et_2O ; the green solid product (yield: 0.5 g, 60 %) was dried in vacuum. Ms: (ESI) m/z 873.97 (871) $[\text{M}+2]^+$, Anal. Calcd (found) for $\text{C}_{28}\text{H}_{32}\text{N}_8\text{O}_{12}\text{Cl}_2\text{Cu}_2$: C, 38.58 (38.45); H, 3.67 (3.75); N, 12.86 (12.90); Cu, 14.58 (14.45).

Synthesis of $[\text{Cu}_4(\text{L})(\text{phen})_2](\text{ClO}_4)_4$, (6)

In EtOH (10 mL), a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (750 mg, 2 mmol) was added to the dinuclear copper (II) complex (5) (870 mg, 1 mmol) in 25 mL of EtOH, and this mixture was refluxed with stirring for 2 h. Then, the separated solution of 1,10-phenanthroline monohydrate (360 mg, 2 mmol) in EtOH was successively added to the resulting mixture, which was boiled under reflux for 5 h. The dark- brown product 1.1 g, (70%) was filtered-off, washed with EtOH, and dried in vacuum. Ms: (ESI) m/z 1558.35(1556), $[\text{M}+2]^+$, Anal. Calcd (found) for $\text{C}_{52}\text{H}_{48}\text{N}_{12}\text{O}_{20}\text{Cl}_4\text{Cu}_4$: C, 40.10 (40.15); H, 3.08 (3.10); N, 10.79 (10.70); Cu, 16.32 (16.25).

Result and Discussion

Bis-[(2E,3E,2'E)-3,3'-(1,2-phenylene-dinitrilo)dibutan-2-one dioxime], (H_4L) (3) were prepared in EtOH by reacting biphenyl-3,3',4,4'tetraamine (1) with butane-2,3-dione oxime (2) (Figure 1). The structures of the ligand and the complexes were established from their ^1H - and ^{13}C -NMR, IR, Uv-vis spectral data, elemental analyses, and magnetic susceptibility studies (Tables 1-3). In the proposed structure of tetraoxime ligand (H_4L), containing N_4 units were available for the complexation of metal ions in tetragonal coordination geometry. In this coordination mode, a square-planar Ni(II) and Cu(II) complexes (4-5) were obtained through the reaction of the ligand and the $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and/or $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ solution in the EtOH (1:2 ligand:metal ratio)

The ^1H -NMR spectra of a DMSO- d_6 solution of tetraoxime ligand (3) showed well resolved signals (Table 1). In the ^1H -NMR spectrum of the tetraoxime ligand (3) were observed 4 singlets at 1.90 (12H), 2.49 (6H), 2.70 (6H), and 11.70 (4H) p.p.m., corresponding to the CH_3 -1/ CH_3 -14, CH_3 -4, CH_3 -13, and -OH protons of oxime groups resonances, respectively. The oxime proton signals at 11.70 p.p.m. disappeared on deuterium exchange.¹⁻⁴ The 11 resonances observed in the ^{13}C -NMR spectra of (H_4L) were also consistent with the proposed formula (Table 1). The ^1H - and ^{13}C -NMR spectral data supported the proposed structures

and indicated the formation of the ligand, H₄L. The ¹H-NMR integral intensities have supported the proposed structure.¹⁻⁴

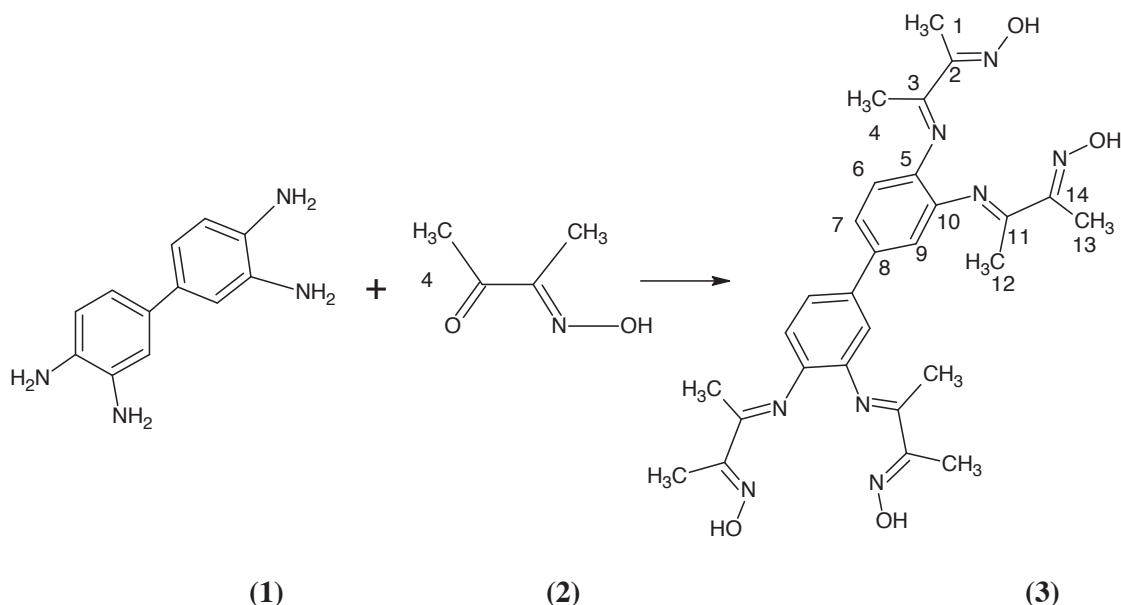


Figure 1. The synthesis route of the tetraoxime ligand.

Table 1. ¹H-, and ¹³C -NMR data for H₄L.

	CH ₃ -1/ CH ₃ -13	CH ₃ -4	CH ₃ -12	Ar-H	=N-OH	C-2, C-14	C-3, C-11
¹ H-	1.90(s. 12H)	2.49(s. 6H)	2.70(s. 6H)	8.03-8.38(m. 6H)	11.70(s., 4H)	-	-
¹³ C-	9.14	20.86	22.64	125.75, 127.94, 128.61, 139.15, 140.10, 142.25	-	154.23	152.88

In general, the complexes exhibited very comparable IR features suggesting that they were of similar structure. Relevant bands were given in Table 2. In the IR spectrum of ligand (3), the O-H, C=N, and N-O stretching vibrations were observed at 3274, 1632, and 977 cm⁻¹ respectively.¹⁻⁴ Complex (4) had the O-H, C=N, and N-O stretching vibrations at 3423, 1614, and 989 cm⁻¹, respectively.¹⁻⁴ In the IR spectrum, intramolecular hydrogen band was observed at 1730 cm⁻¹ for complex (4), at 1700 cm⁻¹ for complex (5), a broad singlet band due to O··H-O intramolecular hydrogen bond.³⁴ Complexes (4-6) (Figure 2) had a strong broad band centred *ca.* at 1080, 1115, and 1140 cm⁻¹, and a sharp band at 625 cm⁻¹ featuring typical characteristics of ionic perchlorates[1-8]. The complex (6) showed strong band at 833 cm⁻¹ and weak band at 786 cm⁻¹, attributable to 1,10-phenanthroline units.³⁵ The azomethine vibration of the ligand at 1632 cm⁻¹ was shifted to lower frequencies after complexation; 1614, 1615, and 1612 cm⁻¹ for complexes 4-6, respectively. This clearly indicated coordination of the tetraoxime ligand through the oxime and azomethine nitrogen.^{1-4,36}

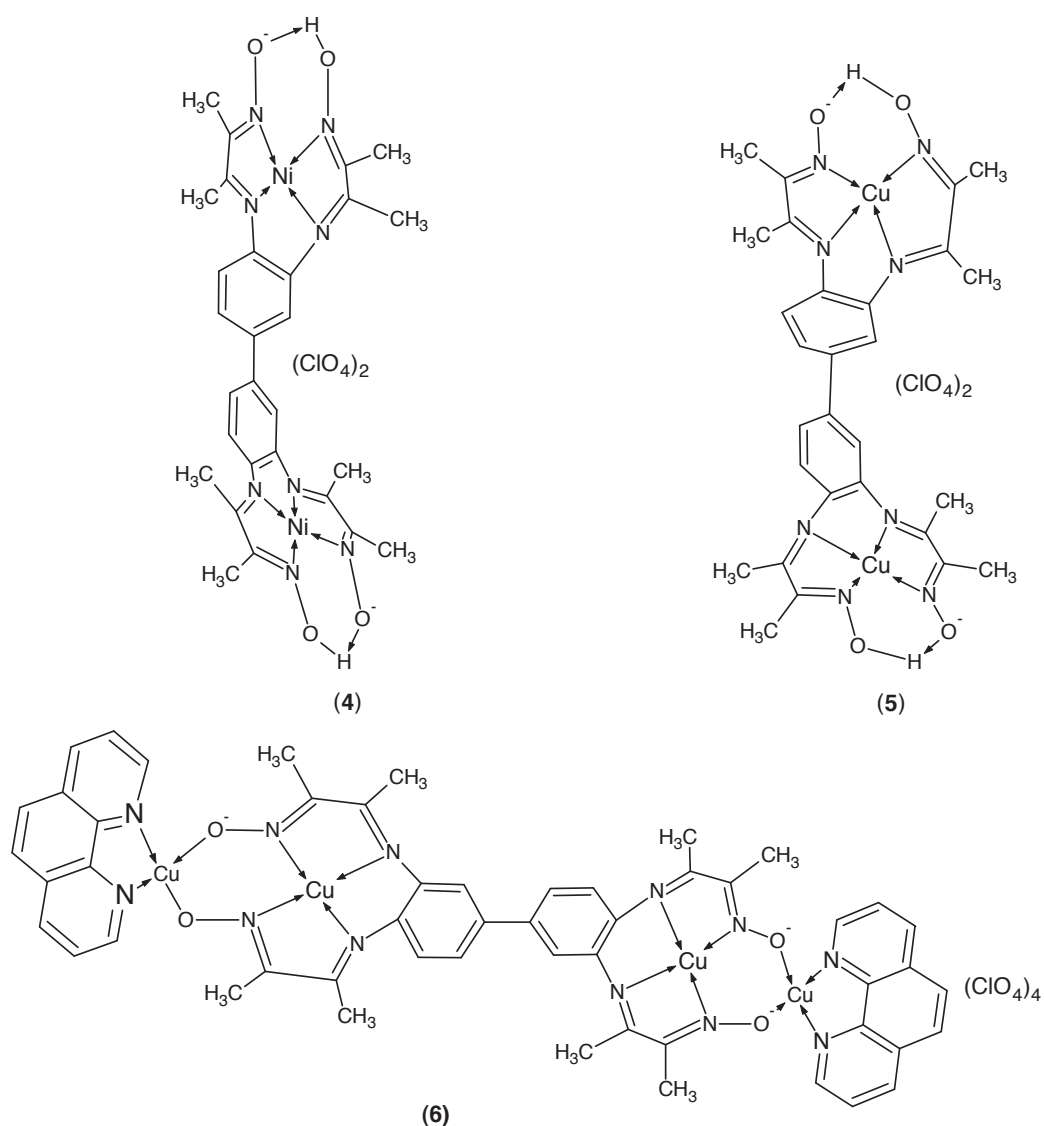

Figure 2. Proposed structure for the metal complexes.

Table 2. Characteristic IR bands of the ligand and its metal complexes (in cm^{-1}).

Compound	$\nu(\text{O-H})$	$\nu(\text{C=N})$ azomet-hyn	$\nu(\text{C=N})$ oxime	$\nu(\text{N-O})$	$\nu(\text{ClO}_4^-)$	H-O...H
H_4L , (3)	3172-3274	1632	1485	977	-	-
$\text{Ni}_2(\text{H}_2\text{L})$ (4)	3423	1614	1565	989	-1120-1144- 1086-627	1730
$\text{Cu}_2(\text{H}_2\text{L})$ (5)	3435	1615	1495	995	1116-1144- 1086-625	1700
$\text{Cu}_4(\text{L})(\text{phen})_2$ (6)	3425	1612	1562	988	1186-1159- 1121-611	-

The mass (ESI) of tetraoxime ligand exhibited the molecular ion at m/z 546.64 $[M]^+$, which indicated the formation of the ligand. The molecular ion peak appeared at $(m/z, \text{ESI})$ 862.7 $[M+1]^+$, 873.97 $[M+2]^+$, and 1558.35 $[M+2]^+$ complexes **4-6**, respectively. Furthermore, the metal to ligand ratio of the dinuclear nickel(II) and copper(II) complexes (Figure 3) were found to be 2:1 metal:ligand ratio according to the elemental analyses. The elemental analysis data for the ligand (H_4L) and its metal complexes (**4-6**) were consistent with the general formula.¹⁻⁴

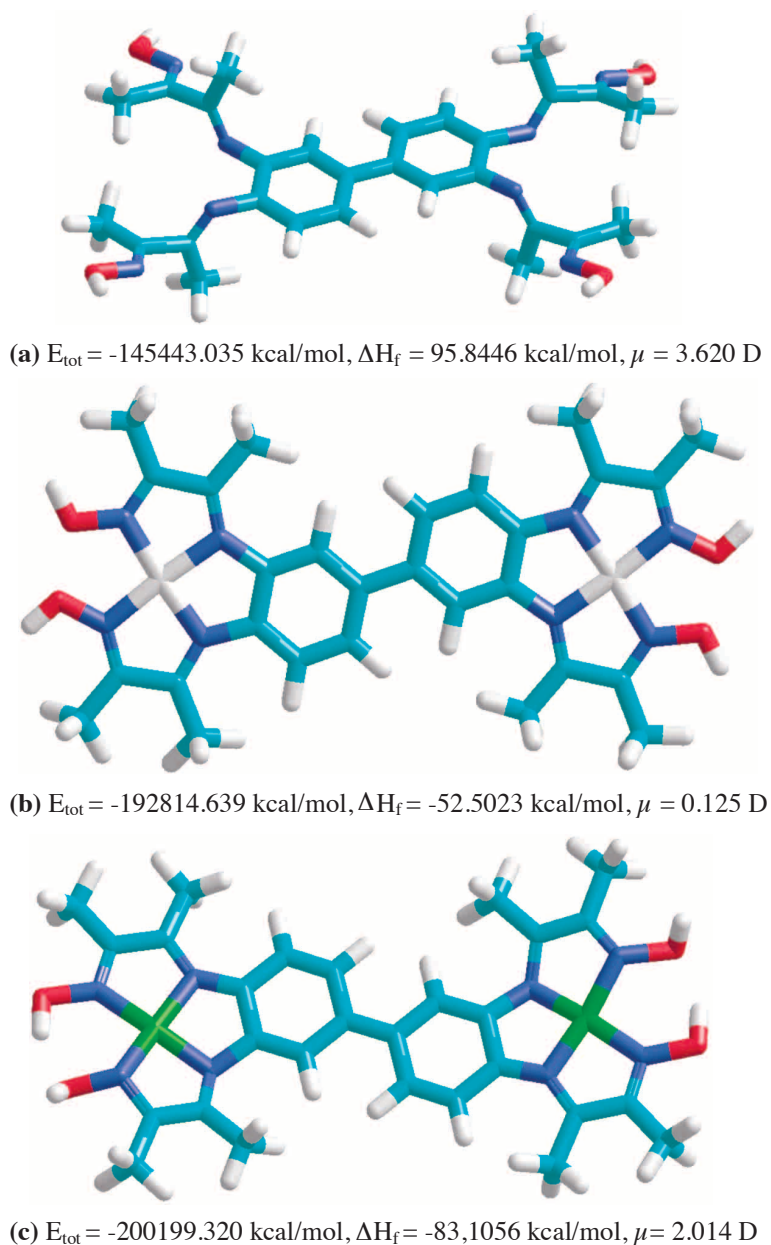


Figure 3. Computer simulation model by semi-empirical PM3 method of the ligand (H_4L) (a); metal complexes, H_2LNi (b), H_2LCu (c).

The electronic spectra of the ligand and its complexes were recorded in DMF at room temperature. The spectra of the ligand and its metal complexes (**4-6**) gave rise to high-energy absorption *ca.* 290 nm. The band of the ligand at *ca.* 290 nm was attributed to $\pi - \pi^*$ transition. The band around 350-380 nm was due to the $n - \pi^*$ transition of the non-bonding electron present on the nitrogen of the imine or oxime group in the ligand and its complexes. The complexes showed less intense shoulder at *ca.* 550-570 nm, which were attributed to d-d transition. The former band was probably due to the ${}^3A_2 \rightarrow {}^3T_2$ (F) for nickel complex and ${}^2T_2 \rightarrow {}^2E$ (G) for copper complex transition of tetragonal geometry.³⁶ The spectra of the complexes showed an intense band at *ca.* 415-430 nm, which could be attributed to a charge transfer (CT) transition of tetragonal geometry.³⁷

The room temperature magnetic moment of the all complexes (**4-6**) showed a normal magnetic moment (Table 3). The magnetic moment data were *ca.* 1.78 and 1.85 B.M. per copper(II) ion corresponding to one unpaired electron of di- and tetranuclear copper(II) complexes (**5, 6**), respectively.^{1-4,10} The magnetic moment studies showed that the dinuclear nickel(II) complex (**4**) was diamagnetic. The complexes (**4-6**), both copper(II) and nickel(II) ions, were square-planar environment formed by the 2 oxime-nitrogen atoms and 2 imine nitrogen atoms of the tetraoxime ligand.¹⁻⁴ In addition, total energy and heat formation (Figure 3) were calculated for ligand and metal complexes (**4, 5**). The metal complexes (**4, 5**) by semiempirical PM3 calculations³³ showed that square-planar geometry was more stable than other geometries (Figure 3).

Table 3. Analytical and physical data of the ligand and its metal complexes.

Comp.	Color	μ_{ef} per metal atom at 297 K (B.M.)	Yield	d-d	C-T	$n - \pi^*$
H ₄ L, 3	Pale-brown	-	73	-	-	380
Ni ₂ (H ₂ L) (4)	Red-brown	Diamag.	58	550	430	365
Cu ₂ (H ₂ L) (5)	Deep-green	1.78	60	570	415	375
Cu ₄ (L)(phen) ₂ (6)	Dark- brown	1.85	62	565	420	360

As a conclusion, in the present study, we demonstrated the preparation of a new tetraoxime ligand providing binucleatin N4 donor array moiety, and its homodi-nickel(II) or copper(II) and homotetranuclear copper(II) complexes. The Ni(II) or Cu(II) metal ions were complexed with nitrogen atoms of the oxime imine nitrogen atoms in square-planar geometry. All the spectral data, elemental analyses and semiempirical PM3 calculations supported the formation of the tetraoxime ligand and its copper(II) and nickel(II) complexes in square-planar geometry.

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